ESRF	**Experiment title:** Stability and Morphological Tuning of PbSe Quantum Dot Superlattices	**Experiment number**: 26-02/805
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Introduction – *In situ* GISAXS and XRF measurements were performed at the DUBBLE BM26B beamline with the aim to elucidate the morphological and compositional evolution of supported cubic superlattices of PbSe Quantum Dots (QDs) during (i) thermal annealing and (ii) Al_2O_3 overcoating using Atomic Layer Deposition (ALD). Secondly, the growth of HfO_2 and ZnO via ALD on CdSe/CdS/ZnS and CdSe/CdS QDs was explored, aiming to deposit a continuous protective layer against environmental damaging agents such as oxygen and water.

Experimental – The experiments can be divided in two sets, depending on the type of QDs that were used. **First**, we evaluated the thermal stability of PbSe QDs forming cubic superlattices. Different sizes of QDs and QDs with and without Pb-oleate surface ligands were compared. The samples were annealed in He or 20% O_2 in He (1 bar) up to 375^{o}C (0.2^{o}C/s). Moreover, different thicknesses of Al_2O_3 overcoats were grown via ALD using the trimethylaluminum (TMA) and H_2O process, and their protective and stabilizing effect during thermal treatment was investigated. **Second**, the encapsulation of CdSe/CdS/ZnS (core/shell/shell) QDs in HfO_2 and of CdSe/CdS (core/shell) QDs in ZnO was investigated. HfO_2 was deposited using the Tetrakis(dimethylamido)hafnium(IV) (TDMAHf) and O_3 ALD process. ZnO was grown from Diethyl Zinc (DEZ) and H_2O vapour. The incidence beam energy was set to 14 keV to excite and record the Pb Lα, Se Kα, Cd Lα, Hf Lα and Zn Kα XRF emission lines. At this energy, however, the beam photon flux was only 30% of the flux at 12 keV (used during previous campaigns), limiting the quality of the GISAXS images recorded. To compensate this loss of intensity, the beam size at the sample position was set to 4 mm × 1 mm (H×V). The GISAXS patterns were recorded using the installed PILATUS3 S 1M detector (Dectris®), while the XRF spectra were acquired using a Vortex® detector from the detector pool.

Results

I. PbSe QDs superlattices: Figure 1a shows the evolution of the ratio of Se/Pb XRF intensity measured during heating of a selected PbSe superlattice. The Se/Pb XRF intensity ratio stays roughly constant up to a temperature of ~320 ºC. At higher temperatures, the Se/Pb XRF intensity ratio drastically decreases, pointing to the loss of Se atoms. The same onset temperature for QD degradation, ~320 ºC, was observed for all samples, irrespective of the presence or absence of Pb-oleate surface ligands, the size of the QDs, the presence of an Al_2O_3 coating covering the superlattice, or the annealing in He or a 20% O_2 atmosphere. For the QDs without overcoating, the corresponding GISAXS patterns showed a decrease in intensity of the characteristic scattering signal associated to the superlattice ordering (~q_y = 0.95 nm^{-1}) from about the same temperature (Fig. 1b). However, for the PbSe superlattices overcoated with ALD-grown Al_2O_3 layers, the superlattice ordering remained present up to ~375 ºC, despite the loss of Se. Different thicknesses of protective alumina layers were investigated (i.e. ~10, 20, 30 nm corresponding to 100, 200 and 300 ALD cycles respectively), and only the thickest Al_2O_3 layer (i.e. 30 nm) could partly prevent the Se evaporation from the sample (Fig. 1a).

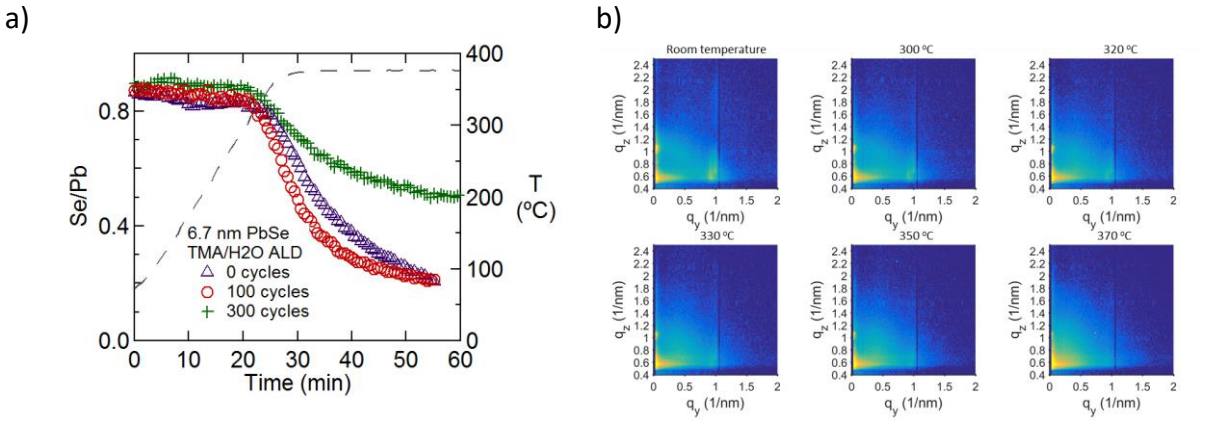

Figure 1. (a) Evolution of the ratio of Se/Pb XRF intensity measured during annealing of PbSe QD superlattices with different thicknesses of Al_2O_3 overcoat under He atmosphere. (b) Representative GISAXS patterns of the PbSe QDs without overcoat recorded during the annealing procedure under He atmosphere, showing the intensity decrease of the characteristic scattering signal of the ordered cubic superlattice (~q_y = 0.95 nm^{-1}) at temperatures above 320°C.

II. HfO_2 and ZnO on QDs: Figure 2a depicts the normalised Hf XRF counts measured during ALD growth of HfO_2 on (i) a native Si/SiO_2 (100) reference substrate, (ii) a monolayer of CdSe/CdS/ZnS QDs, and (iii) a monolayer of the CdSe/CdS/ZnS QDs where the ligands where removed prior to the ALD deposition. The results show that the HfO_2 growth rate is linear and without any incubation period during the first ALD cycles, even on the QDs.
It is known that the ALD growth of ZnO on CdSe/CdS/ZnS QDs via the DEZ/H_2O process is strongly inhibited. However, it can be triggered by pre-exposing the QDs to TMA, as we investigated previously [JPCC 120, 18039, 2016]. Here, we screened different pretreatments to trigger the growth of ZnO on CdSe/CdS QDs. Figure 2b shows the normalised XRF counts of the Zn signal measured during ALD growth of ZnO on (i) a SiO_2 reference, (ii) a monolayer of CdSe/CdS QDs which were exposed to an Ar plasma pretreatment, and (iii) the same QDs exposed to an O_2 plasma pretreatment. Following an initial slower growth, the ZnO growth on SiO_2 (green symbols) reaches a linear growth regime after ca. 20 ALD cycles. A pretreatment of the QDs with an exposure of 5s Ar plasma (red symbols) shows a small increase in the amount of deposited ZnO. However, the growth is not yet triggered and levels off. After an exposure of 4x30s to the Ar plasma, the growth of ZnO really takes off and continues steadily. The influence of O_2 plasma is seen in the black data points. An exposure of 1s O_2 plasma shows again a small increase in the amount of deposited Zn while an exposure of 5s triggers the growth of ZnO. Complementarily, the influence of a pretreatment with TMA, O_3, TDMAHf, and $(CH_2TMS)_2S$ was investigated. Non of this pretreatments triggered the growth of ZnO on CdSe/CdS QDs.

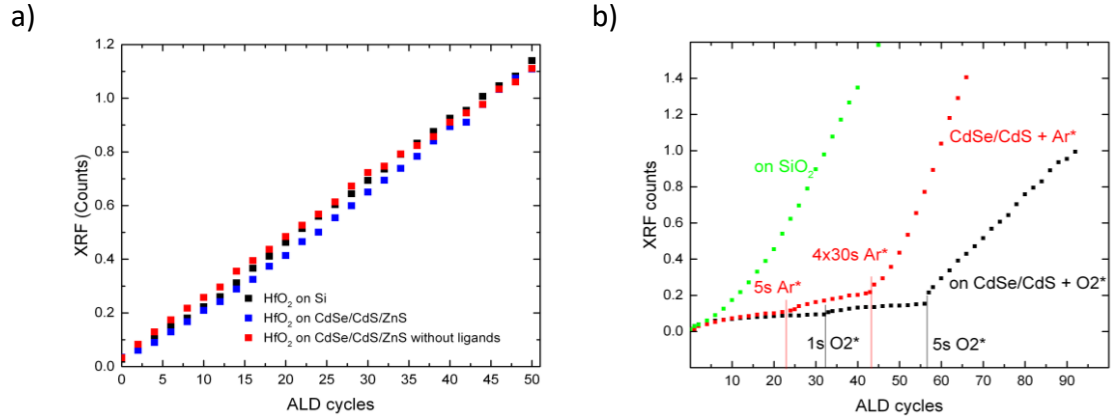

Figure 2. (a) XRF signal of Hf during deposition of 50 ALD cycles on SiO_2, CdSe/CdS/ZnS QDs with organic ligands, and CdSe/CdS/ZnS QDs without organic ligands. (b) XRF signal of Zn during deposition of ZnO on a SiO_2 reference and CdSe/CdS QDs with different plasma pretreatments.

Conclusions – The beamtime at BM26B allowed us to systematically investigate the thermal stability of a series of PbSe QDs. This knowledge will be important input for our ongoing work which explores the use of a temperature treatment to increase the necking between the supported QDs and improve the charge transport of the QD layer. Preliminary results also demonstrated that ALD of HfO_2 is a suitable technique for overcoating CdSe QD-based layers that act as barrier against environmental oxygen and moisture while maintaining the photoluminescent properties of the QDs. Finally, XRF indicated that a plasma pretreatment is required to initiate the growth of ZnO on CdSe/CdS QDs. An investigation of the effect of the plasma pretreatment on the photoluminescent properties of the QDs is ongoing.